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INFRARED SPECTROSCOPY OF $CH_5^+(H_2)$

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ABSTRACTS

The infrared spectrum of $CH_5^+(H_2)$ has been obtained from 2650 cm^{-1} to 4200 cm^{-1} with 0.2 cm^{-1} resolution. In the spectrum two peaks were found: one broad and asymmetric band in the 2800 - 3150 cm^{-1} region and one rotationally resolved band in the 4050 - 4120 cm^{-1} region. They were assigned as the C-H and H-H stretching bands of the CH_5^+ moiety of $CH_5^+(H_2)$ and as the H-H stretching band of the H_2 moiety, respectively. The observed frequency range of the C-H and H-H stretching modes agree well with ab initio predictions on CH_5^+. The broad and asymmetric band features would be attributed to the contribution from spectral congestion and hot band transitions, respectively. In this work we modelled the structure of $CH_5^+(H_2)$ based upon the results of this work and other works on related cluster ions. Using the model structure of $CH_5^+(H_2)$ we were able to find the best fit simulated spectrum to the observed H-H stretching band of the H_2 moiety with improving the model structure. In the spectrum of the H-H stretching band of the H_2 moiety the evidence of tunneling splittings and hot band transitions was also found.

INTRODUCTION

There has been a considerable interest in the CH_5^+ and protonated alkanes since they play an important role as intermediates in chemical reactions, especially electrophilic reactions. The carbonium ions have been known to form triangular three center two electron bond by single bonds acting as σ-donors.[1] The simplest carbonium ion is CH_5^+. As an analytical species it is typically used as a source in chemical ionization mass spectrometry.[2] This species is also of astrophysical interest in that it may serve as an indicator for methane in galactic molecular clouds.

Several theoretical calculations have been carried out on the structure of CH_5^+.[3-7] They consistently suggested that C_s symmetry with a three center two electron bond is the ground state structure, especially the eclipsed C_s symmetry structure. However, the C_s, C_{2v}, C_{4v}, and D_{3h} symmetry structures become close in energy when correlation corrections are included.

In order to get information on the structure of CH_5^+, several experimental works such as measurement of thermochemical data, $\Delta H^\circ_{n-1,n}$ and $\Delta S^\circ_{n-1,n}$ have been done for the clustering reactions $CH_5^+(CH_4)_{n-1} + CH_4 = CH_5^+(CH_4)_n$(n=1-9) using a pulsed electron beam mass spectrometer.[8,9] They observed an irregular decrease in the values $-\Delta H^\circ_{n-1,n}$, $-\Delta S^\circ_{n-1,n}$ between n=2 and 3, indicating that the first two CH_4 ligands are accommodated by the core ion CH_5^+ much more favorably than those with n≥3. This experimental result is compatible with a three center two electron bond structure for CH_5^+ with C_s symmetry since the two acidic H atoms of the three center two electron bond would give the most favorable sites for the accommodation of the first two CH_4 ligands.

In order to understand the intramolecular dynamics of the CH_5^+, the frequencies and

intensities of the vibrational modes have been calculated for the two C_s symmetry structures at various theoretical levels with appropriate scaling.[10,11] However, since the CH_5^+ ion is one of the nonrigid ions which may have large anharmonic mixing of modes due to the coupling between high frequency motions and low frequency motions, the harmonic frequencies predicted from the equilibrium geometries would be of limited use. But, there has been no way of testing these results by comparing with experimental data due to the absence of any spectroscopic measurement on the CH_5^+ and its related clusters in spite of its importance.

In order to get better understanding on the structure and the intramolecular dynamics of the CH_5^+ ion we have been studying the CH_5^+ ion and its solvated clusters $CH_5^+(X)_n$(X= H_2, CH_4, rare gases, etc) using infrared laser spectroscopy based upon vibrational predissociation. This technique has advantage of zero background and very high sensitivity which is important for the study of weakly bound clusters which can not be generated in large numbers.

As the first step of this study, we have been studying the $CH_5^+(H_2)$ ion which has at least two advantages for this study. First of all, this cluster ion is a weakly bound cluster so that we can get information on the structure of the CH_5^+ ion by observing rovibrational spectra of the H-H stretching mode of H_2 moiety which may not be strongly coupled to the vibrational modes of the CH_5^+ moiety. In a sense the H_2 plays an role of a messenger. Second, the ion $CH_5^+(H_2)$ has low binding energy so that it can be vibrationally predissociated by single infrared photon absorption, which allow us to detect photon absorption by $CH_5^+(H_2)$ easily. From the spectra of the CH_5^+ moiety of the $CH_5^+(H_2)$ we can extract some information on the dynamics of the CH_5^+ ion itself.

As an initial survey, we searched the frequency region from 2650 cm^{-1} to 4200 cm^{-1} with 0.2 cm^{-1} resolution for the $CH_5^+(H_2)$ ion.

EXPERIMENTAL

The experimental apparatus used in this work has been described previously.[12-15] Briefly, the $CH_5^+(H_2)$ ions were produced from a high pressure corona discharge source and subsequent supersonic expansion through a 75 μm nozzle. The corona discharge was maintained in 100-150 torr of gas with UHP H_2 and UHP CH_4(2000 : 1 ratio) flowing past a 1.0 kV potential from the discharge tip of the needle to the source body maintained at approximately 350 V above ground. The discharge current under these conditions was around 30 μA. The source could be cooled from the outside the machine by contact with a liquefied gas reservoir and was maintained at approximately -40°C. Typical pressures in the source chamber are around $4x10^{-5}$ torr while running the experiment. To prevent internal excitation and dissociation of the ion clusters through collisions with the background gas in the expansion the potential of the skimmer was maintained within 1 V of that of the source body.

After the skimmer, the ion beam enters a second differential pumping region containing collimating and focusing lenses. The pressure in this region is typically an order of magnitude lower than that of the source region. The beam is directed into a 60° sector magnet mass analyzer through a third differentially pumped region maintained at 10^{-8} torr.

The mass-selected beam is then bent 90° in a dc quadrupole field, decelerated to less than 0.5 eV, and focused into a rf octapole ion trap through an entrance aperture lens. The ions are usually trapped here for ~1.5 msec before IR irradiation. Usually, 1,500 ions are trapped, not enough to allow measurement of direct photon absorption.

The trapped, mass-selected clusters are then vibrationally excited by a pulsed, tunable infrared laser. The tunable infrared laser is a Quanta-Ray IR WEX. The infrared wavelength

is generated in a $LiNbO_3$ crystal that takes the difference of a Lambda Physics pulsed dye laser(Model FL3002E) output and a Continuum Nd-YAG laser 1.06 μm output. The IR resolution is 0.2 cm^{-1} and 0.04 cm^{-1} without and with the intracavity etalon in the dye laser, respectively. Pulse duration is 6 nsec with 20 Hz repetition rate and with 0.5-2 mJ/pulse in the 2650-4200 cm^{-1} region, which is scanned in this work.

If the clusters absorb one or more IR photon(s) in the usual tuning range of 2650-4200 cm^{-1}, the clusters $CH_5^+(H_2)$ vibrationally predissociate into CH_5^+ and H_2. The potential on the exit aperture is lowered 0.5 msec after the laser pulse, extracting cluster ions of all masses from the trap. These ions are filtered by a second mass analyzer, a quadrupole mass spectrometer tuned to pass only the daughter ions, CH_5^+.

Daughter ions are counted by means of a Daly ion detector[16] for each laser shot. Background daughter ions resulting from the decay of metastable parent ions in the rf ion trap are monitored in a separate cycle with the laser off at each wavelength and subtracted from the laser on signal.

Laser power is monitored at each data point, and spectra are normalized for the tunable infrared power by using a simple linear power dependence. For a typical experiment, signals are averaged for about 2,000 laser shots at each wavelength in the 2700-3300 cm^{-1} and 4000-4200 cm^{-1} regions.

In this experiment, it was seen that the composition of ions in the beam was strongly dependent on the mixing ratio of H_2 and CH_4 gases, the source temperature and the source pressure behind the nozzle. The optimum conditions for the $CH_5^+(H_2)$ were obtained at the ratio of H_2:CH_4 = 2000:1, -40°C and 100 torr, respectively. Fig.1 shows the mass spectrum obtained under these conditions.

Two significant vibrational bands were found in the frequency region scanned in this work: one broad band in the 2800 - 3150 cm^{-1} region and one rotationally resolved band in the 4050 - 4120 cm^{-1} region. These frequency ranges correspond to those for the C-H stretching modes in CH_5^+ and the H-H stretching mode in H_2, respectively.

As shown in Fig.2, the bands which are centered at 2966 cm^{-1} are very broad(observed bandwidth $\equiv$ 115 cm^{-1}), and slightly asymmetric. According to the ab initio results on the vibrational frequencies of CH_5^+ ion,[10,11] these broad bands can be assigned to three C-H stretching bands and one H-H stretching band of the CH_5^+ moiety.

Fig.3 shows the H-H stretching band, possibly of the H_2 moiety of the $CH_5^+(H_2)$ ion. As shown in Fig.3, the spectrum has band origin at 4077.4 cm^{-1} , which is red-shifted 83.6 cm^{-1} from the vibrational origin of unbound H_2 monomer at 4161 cm^{-1}. And it has very clear P,Q,R branches which may indicate the parallel transition band of a symmetric top molecule. The rotational line spacing was measured to be approximately 1.5 cm^{-1}. Also, the P-branch region seems to be slightly compressed, whereas the R-branch region expanded. Another interesting feature is that each rotational line seems to be splitted even though the signal-to-noise ratio and the resolution are not good enough to determine the exact origin of the splitting.

DISCUSSION

A. Modelling of $CH_5^+(H_2)$ structure

Since no ab initio quantum calculations on the $CH_5^+(H_2)$ structure have been carried out,

it was necessary to model the structure of $CH_5^+(H_2)$ for the comparison with our observed spectra, of this work and other previous results on related cluster systems such as H_n^+,[17] $CH_5^+(CH_4)_n$,[8,9,18,19] $CH_3^+(Ar)_n$,[20] etc.

In our previous work on the hydrogen cluster ions H_n^+(n= 5,7,9,11,13,15),[17] the hydrated hydronium cluster ions $H_3O^+(H_2O)_n(H_2)_m$,[21] and $C_2H_7^+$ [22] we were able to correlate the frequency shift of the H-H stretching mode from free H_2(4161 cm^{-1}) with the binding energy of the H_2 moiety to the rest of the ion. As some of results are shown in Table I, the larger the frequency shift, the more strongly the H_2 moiety is bound. The $CH_5^+(H_2)$ ion has the smallest frequency shift(-83.6 cm^{-1}) among these cluster ions, which means that $CH_5^+(H_2)$ is the most weakly bound cluster ion. From Table I the binding energy between CH_5^+ and H_2 is estimated to be much less than 3 kcal/mol, possibly 1 ~ 2 kcal/mol. This indicates that the interaction between the CH_5^+ moiety and the H_2 moiety could be weak electrostatic interaction due to ion-induced dipole interaction, rather than strong charge transfer interaction or such a covalent interaction as in the three center two electron bond of the CH_5^+(binding energy ≡ 40 kcal/mol[10]). Therefore, the ground state structure of the $CH_5^+(H_2)$ ion seems to be composed of CH_5^+ and a weakly bound H_2 moiety.

The next question is the location of the binding site of the CH_5^+ moiety to the H_2 moiety. Several experimental and theoretical works have been done on the stabilities and structures of $CH_5^+(CH_4)_n$ cluster ions (n= 0 to 9).[8,9,18,19] It has been concluded that two acidic H atoms participating in the three center two electron bond of CH_5^+ would be the most favorable binding sites for the first two CH_4 ligands. By analogy between $CH_5^+(H_2)$ and $CH_5^+(CH_4)$, for $CH_5^+(H_2)$, the binding site on the CH_5^+ moiety would be also one of two acidic H atoms which form the three center two electron bond. The overall possible ground state structure of $CH_5^+(H_2)$ is shown

in Fig.4.

In the determination of the $CH_5^+(H_2)$ structure, we noticed that the previous works on ab initio structures of CH_5^+ and $CH_5^+(CH_4)_n$ suggest that there would be very little change in the geometrical parameters of the CH_5^+ moiety of $CH_5^+(CH_4)$ from those of the CH_5^+ by the attachment of CH_4 ligand to the CH_5^+ moiety.[19] For example, H5-H6 = 0.86 Å(0.85), ∠H5-C-H6 = 41°(40°), C-H5 = 1.22 Å(1.24), and C-H6 = 1.24 Å(1.24) for the structure of the CH_5^+ moiety shown in Fig.4, values in parentheses referring to isolated CH_5^+. Moreover, the $CH_5^+(H_2)$ ion has much less binding energy than $CH_5^+(CH_4)$(binding energy = 6.87 kcal/mol), so it may have even less change in the geometrical parameters of the CH_5^+ moiety than $CH_5^+(CH_4)$ does. Therefore, in the first approximation, the geometrical parameters of the ab initio structure of CH_5^+ can be directly used as those of the CH_5^+ moiety in $CH_5^+(H_2)$. In addition, for this assumed structure, if we replace the CH_3 part of the CH_5^+ moiety by an H atom, the structure of $CH_5^+(H_2)$ becomes similar to that of H_5^+.[17] From this structural similarity between $CH_5^+(H_2)$ and H_n^+(n= 5,7,9,11,13,15), it is possible to get information on the distance between the CH_5^+ moiety and the H_2 moiety, and the H-H bond distance of the H_2 moiety by finding one of H_n^+ cluster ions which has a similar frequency shift for the H-H stretching mode from free H_2 as $CH_5^+(H_2)$ does. In this work the geometrical parameters for H_9^+ were used.[23] Using this model for $CH_5^+(H_2)$ the following rotational constants were obtained: A= 4.2 cm^{-1}, B= 0.87 cm^{-1}, C= 0.86 cm^{-1}.

B. The H-H stretching band(4050 cm^{-1} - 4120 cm^{-1})

Fig.3 shows the H-H stretching vibrational band of the H_2 moiety. The spectra have very clear P, Q, and R rotational branches, which may indicate the parallel transition band of a symmetric top or nearly symmetric top molecule. This result is consistent with our predicted

$CH_5^+(H_2)$ structure which has asymmetry parameter κ = - 0.99. However, the spacing between each rotational line was measured to be approximately 1.5 cm^{-1}, which is somewhat different from the 2B value(1.73 cm^{-1}) predicted in Section A. The difference between two results are possibly due to our underestimation of the distance between the H_2 and the nearest H atom. Actually, the H_9^+ ion of which geometrical parameters were used for our calculation has almost twice as large frequency shift as $CH_5^+(H_2)$ ion does(-141 cm^{-1} vs -83.6 cm^{-1}).[17] In addition, according to recent ab initio calculation on the structures of hydrogen ion clusters[24] the distance(D) between the H_2 and the nearest H atom significantly increases as the clusters increase in size whereas the bond length(P) of H_2 doesn't change so much. In other words, the distance D is very sensitive to difference in the structures of the rest of the ion. For example, at the TZP MP4SDTQ level, for H_5^+, D = 1.21 Å, P = 0.77 Å; for H_7^+, D = 1.54 Å, P = 0.76 Å; for H_9^+, D = 1.64 Å, P = 0.75 Å. Therefore, for the $CH_5^+(H_2)$ ion, we can expect a longer distance due to the weaker interaction. Using the distance (D) as a variable it is possible to estimate the distance(D) so that our calculated rotational constant B becomes equal to 0.74 cm^{-1}, the B value which is determined from the best fit between the observed spectra and the simulated spectra. The distance(D) was found to be approximately 2.0 Å.

Fig.5(b) shows the best fit simulated spectra assuming a prolate top structure for $CH_5^+(H_2)$ with rotational constants A = 4.2 cm^{-1}, B = C = 0.74 cm^{-1} for the ground vibrational state and $A' = 4.2$ cm^{-1}, $B' = C' = 0.746$ cm^{-1} for the excited vibrational state, together with our observed spectra shown in Fig.5(a). By comparing two spectra, rotational J quantum numbers are assigned to the observed spectra. Fig.6 shows the expanded picture of the spectra near the Q-branch shown in Fig.5. It is easily seen that although two spectra agree reasonably well there are at least two significant differences between them. First of all, there exist two anomalously

intense peaks in the observed spectra between Q and R branches(marked with asterisks). Second, most of rotational lines seem to have substructures of splittings. For two anomalously intense peaks, there could be several possible explanations. Among them one possibility is that these peaks would be parts of the Q-branch progressions of a perpendicular band. For accidental symmetric top molecules like $CH_5^+(H_2)$, it is very often for a parallel transition band to have a small perpendicular band component in it.[25] However, in this case the spacing between two intense lines should be equal to the 2(A - B) value, i.e. 6.92 cm^{-1}, but the spacing turned out to be 3.4 cm^{-1}. There is a significant difference between two values. So, this may not be valid explanation for the existence of the two additional peaks. The other possibility is that these bands would be hot bands of ions vibrationally excited before IR irradiation. The existence of hot band transitions has been observed before in our group for weakly bound clusters such as the hydrogen ion clusters under similar experimental conditions with corona discharge ion source.[17] This explanation is also consistent with that for the asymmetric feature of the 2800 - 3150 cm^{-1} band which will be discussed in Section C. If these peaks were hot bands the low frequency vibrational modes such as van der waals stretching mode in which the H_2 moiety is directly involved would be more likely responsible for the hot band transitions rather than other high frequency modes or low frequency modes which belong to the CH_5^+ moiety. There could be at most five such low frequency modes which came from three translational and two rotational degrees of freedom of H_2(for example, one rotational degree of freedom becomes an internal rotational mode of H_2 about one internal axis of the CH_5^+ and one translational degree of freedom becomes the van der waals stretching mode). They seem to be strongly coupled to the H-H stretching mode and also easily excited during the clustering reaction in the ion source since they are closely related to the reaction coordinates of association and dissociation reactions between

the CH_5^+ and the H_2. On the other hand, for higher frequency modes of which lowest frequency is that of ν_8 mode of the CH_5^+ moiety(~966 cm^{-1}, according to the ab initio calculation[10]), they are not likely to be involved in the hot band transitions because the $CH_5^+(H_2)$ seems to have very small binding energy(i.e. 1 ~ 2 kcal/mole) and if they become vibrationally excited in the ion source most of the excited $CH_5^+(H_2)$ ions will be predissociated during trapping inside the octapole ion trap or during flight time from the ion source to the octapole trap due to the higher internal energy than the binding energy. Therefore, the high frequency modes may not be involved in the hot band transitions. It is also interesting to notice that two intense lines are located at the higher frequency side relative to the main Q-branch. This can be qualitatively explained by the following: If the van der waals mode were responsible for these hot band transitions and became excited before IR irradiation the equilibrium bond distance between the H_2 and the nearest H atom would be increased, so the interaction between the H_2 and the CH_5^+ moiety become weaker due to the longer distance. This will result in less frequency shift in the H-H stretching mode, compared with the normal transition bands, and the peaks will appear at the higher frequency side.

Another thing to notice is that the P-branch looks slightly compressed whereas the R-branch slightly expanded with higher baseline. This could be in part due to the contribution of the hot bands which mainly develop at the main R-branch side. Actually, by summing the full simulated rotational spectra of the hot bands together with the main rotational spectra it was possible to have better match between two spectra, especially for the higher baseline at the R-branch side in the observed spectra. Furthermore, the compressed P-branch and the expanded R-branch features are typical for nonrigid cluster systems which have higher rotational constants in excited vibrational state than in ground vibrational state. Typically, this is opposite to the case

of rigid systems. This is evident in Fig.5(b), where shows the simulated spectra which have the best fit with higher excited state rotational constants. The larger rotational constants in the excited state could be explained as following: For nonrigid systems like $CH_5^+(H_2)$, when H_2 is vibrationally excited the equilibrium bond distance increases, which induces a stronger interaction between the H_2 and the CH_5^+ due to the increased polarizability of the H_2 moiety. Finally, this results in a shorter bond distance between the H_2 and the nearest H atom, so larger rotational constants, especially in B and C rotational constants.

The other difference between two spectra is that each rotational line of the observed spectra has substructure of splittings. The spacing of splitting is about 0.4 cm^{-1}, which is only twice as large as the laser resolution. This may indicate that some tunneling motions occur in this flexible cluster ion, even though the spectral resolution and the signal-to-noise ratio of the spectra are not good enough to verify this possibility. Recently, the similar line splittings have been observed for both the hydrogen ion clusters $H_3^+(H_2)_n$[17] and their isotope exchanged clusters $D_3^+(D_2)_n$[26] in our group and have been explained in terms of tunneling splittings. In fact, the tunneling splittings could be expected especially for $CH_5^+(H_2)$ since all five hydrogen atoms of the CH_5^+ moiety are interchangeable due to very low potential barriers, which will be discussed in Section C. However, at this point, it is still unknown what kind of tunneling motions occur in $CH_5^+(H_2)$. In order to determine the origin of the splittings it is necessary to use a higher resolution and to improve the signal-to-noise ratio of the spectra and also to study the isotope exchanged clusters of $CH_5^+(H_2)$.

C. The C-H stretching and H-H stretching bands in CH_5^+ moiety(2800 - 3150 cm^{-1})

As shown in Fig.2 these bands have very broad band feature with observed bandwidth of

~115 cm^{-1} and also asymmetric feature especially near the lower frequency side. In Section A the results on correlation between the binding energy and the frequency shift of the H-H stretching band indicated that the H_2 moiety is very weekly bound to the CH_5^+ moiety, so the H_2 moiety doesn't seem to substantially modify the structure and the vibrational motions of the CH_5^+ moiety from those of isolated CH_5^+. Therefore it may be possible to compare these observed bands with various ab initio results[10,11] on the corresponding vibrational bands of the CH_5^+ ion assuming that there is only slight or negligible difference in vibrational frequencies between two ions. This result will indicate what kinds of theoretical treatments give more close prediction to our results and how much discrepancy there is between experimental and theoretical vibrational frequencies. This will give the first opportunity for the comparison with the theoretical predictions on the CH_5^+ ion. However, if the binding between CH_5^+ and H_2 occurs through one of two H's which are forming the three center two electron bond of CH_5^+, it is likely that especially the H-H stretching band of CH_5^+ moiety may have somewhat significant difference in frequency from that of the CH_5^+ ion . But, for the three C-H stretching bands of the CH_5^+ moiety which is not directly coupled to the binding the above assumption seems to be valid.

In 1985 DeFrees and McLean carried out ab initio calculation on the vibrational frequencies of one C_s symmetry structure at the HF/6-31G* and the MP2/6-31G* levels using uniform scaling.[11] Later, Komornicki and Dixon also carried out ab initio calculation on the vibrational frequencies and intensities analytically at the SCF level for two C_s symmetry structures of the CH_5^+ ion.[10] According to Komornicki and Dixon two C_s symmetry structures are very close in energy. In fact, the eclipsed C_s structure is lower in energy only by ~25 cm^{-1} than the staggered C_s structure. The staggered C_s structure is a transition state along the internal rotor path of the H_2 about the pseudo threefold axis of the CH_3^+ group, suggesting that this

internal rotor is a nearly free rotor. Table II lists the ab initio results on CH_5^+ ion mentioned above as well as our results on $CH_5^+(H_2)$ ion. As seen in Table II, the DeFrees and McLean's HF/6-31G* results are more close to our results than other three results. In general other three results are predicting somewhat larger vibrational frequencies for three C-H stretching bands of CH_5^+. It is also interesting to notice that according to DeFrees and McLean the uniformly scaled HF/6-31G* frequencies are overall in good agreement with experimental frequencies for 30 molecular ions tested. For example, for CH_3^+ ion the C-H asymmetric stretching band was predicted to be 3090 cm^{-1} which is close to the experimental value, i.e. 3107 cm^{-1}. In Fig.2 the line spectrum shows the predicted C-H stretching bands and H-H stretching band of the CH_5^+ moiety using the uniformly scaled HF/6-31G* vibrational frequencies for CH_5^+ and also using vibrational intensities of the corresponding bands predicted by Komornicki and Dixon. As seen in Fig.2 all lines fit reasonably well with our observed bands predicting slightly higher frequencies for three C-H stretching bands than our observed frequencies. This may be due to red shifts in frequency for $CH_5^+(H_2)$ possibly from a weak charge transfer effect between H_2 and CH_5^+ with respect to that for CH_5^+ ion. It is also interesting to notice that the H-H stretching band also matches with one broad shoulder peak in the observed spectrum, even though there may exist some contribution to this broad band from the hot band transitions of vibrationally hot ions. In this work we tried to cool down the $CH_5^+(H_2)$ ions by using low source temperature(-40°C) and as high source pressure as possible($\geq$ 100 torr) as well as by trapping the $CH_5^+(H_2)$ ions inside the octapole ion trap for long time(~1.5 msec) in order to get rid of metastable ions formed before IR irradiation. However, as illustrated in the previous section, there are still significant contributions from vibrationally hot ions with especially low frequency modes excited. Similarly, the contribution from vibrationally hot ions may also exist in these bands, resulting in

the overall band shape becoming asymmetric especially in the lower frequency side. Such asymmetric band feature has been also observed before for weakly bound cluster ions such as the hydrogen ion clusters H_n^+ by Okumura et al[17] of our group.

Why are these bands so broad? There are several possible explanations for this. One possibility is that the spectra were very congested. First of all, there exist four vibrational bands in this frequency range, i.e. three C-H stretching and one H-H stretching bands. Each vibrational band become rotationally splitted with line spacing of 2B = 1.48 cm^{-1}. In addition, in $CH_5^+(H_2)$, two H_2 groups are likely to form nearly free or slightly hindered internal rotors with very low potential barriers about one internal axis of CH_5^+ moiety and one pseudo 3-fold axis of CH_3^+, respectively. Particularly, if the ions were internally hot with low frequency vibrational modes excited, it would be possible for the ion to have all the different frequencies available along those internal rotor paths for these vibrational modes. As a result, the bands may considerably spread out. Another contribution to the spectral congestion may come from tunneling splittings. According to the ab initio results on the energetics of CH_5^+ structures, the energy difference is very low(1.1[6] or 0.2 kcal/mole[7]) between the eclipsed C_s structure and the C_{2v} structure which is a transition state between two eclipsed C_s structures. Also, as mentioned before, the eclipsed C_s structure is very close in energy($\leq$ 0.1 kcal/mole[6,10]) with the staggered C_s structure which is a transition state along the internal rotation path of H_2 about the pseudo 3-fold axis of CH_3^+. Now it is readily seen that combination of the above isomerizations can lead to exchange of any pair of hydrogen atoms in the CH_5^+ moiety of $CH_5^+(H_2)$ ion assuming that there exist only weak interactions so that the CH_5^+ moiety is very close to CH_5^+ ion itself in nature. Thus, all five H atoms can be permuted, compared to a rigid structure, and the CH_5^+ moiety can access 5! = 120 C_s potential minima. The large amplitude motions greatly increase the number of states, which

results in many splittings of each vibrational band in the spectra even though the expected splittings will be reduced from nuclear spin considerations. The occurrence of such tunneling splittings has also been reported for the hydrogen ion clusters H_n^+.[17]

Another possibility could be lifetime broadening . This would require that the linewidth be order of the rotational spacing of 1.48 cm^{-1}, which corresponds to approximately a few picosecond lifetime. Such a lifetime broadening has been also observed in the vibrational predissociation spectra of van der waals clusters, e.g. ν_7 mode of ethylene dimer.[27,28] In order to verify this possibility, more works such as lifetime measurement will be necessary.

CONCLUSION

The IR spectra of $CH_5^+(H_2)$ have been presented. These spectra are the first spectroscopic results for the carbonium ion CH_5^+ and its clusters $CH_5^+(X)_n$(X = H_2, CH_4, rare gases, etc.). In the spectra, the C-H stretching and the H-H stretching bands of the CH_5^+ moiety were found as one broad and asymmetric band whereas the H-H stretching band of the H_2 moiety as one rotationally resolved band with clear P-, Q-, and R-branches. Both bands have other interesting spectral features such as splittings and hot band transitions. They were fully discussed by modelling a possible structure of $CH_5^+(H_2)$ based upon our results and other previous results on similar cluster ions.

A clear extension of this work would be to use a higher resolution and improve the signal-to-noise ratio of the spectra, and to study the isotope exchanged clusters of $CH_5^+(H_2)$. Also, theoretical works should be performed for better understanding on the CH_5^+ and the $CH_5^+(H_2)$ ion in the future.

ACKNOWLEDGEMENT

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TABLE I. H-H Stretching Frequencies, Frequency Shifts, and Binding Energies of Hydrogen Cluster Ions H_n^+, $C_2H_5^+(H_2)$, and $CH_5^+(H_2)$.

Ions	H-H Stretching Frequency, cm^{-1}	Frequency Shift,[a] cm^{-1}	Binding Energy, kcal/mol
$H_3^+(H_2)$[b]	3910	-251	6.6 ± 0.3[b,c]
$C_2H_5^+(H_2)$[c]	3964	-197	4.0 ± 0.5[c]
$H_5^+(H_2)$[b]	3980	-181	3.1 ± 0.1[b,c]
$H_7^+(H_2)$[b]	4020	-141	≤ 3.1[b]
$CH_5^+(H_2)$[d]	4077.4	-83.6	?

[a]Relative to the H-H stretching frequency of monomer H_2, 4161 cm^{-1}. [b]Reference 17. [c]Reference 22. [d]This work.

TABLE II. Vibrational Frequencies and Relative Intensities of CH_5^+ and $CH_5^+(H_2)$

Vibrational Normal Modes	Calculated Frequencies with scaling, in cm^{-1}				Observed Frequencies,[c] in cm^{-1}
	Dixon et al[a]		McLean et al[b]		
	e-C_s	s-C_s	HF/6-31G*	MP2/6-31G*	
CH_3 Symmetric Stretching(ν_1)	3119 (50)	3193 (45)	2970	3210	
CH_3 Degenerate Stretching(ν_2)	3066 (60.8)	3074 (64.9)	2933	3091	2800 - 3150 max: 2966 cm^{-1} bandwidth: ~115cm^{-1}
CH_3 Asymmetric Stretching(ν_9)	3189 (67.6)	3103 (79.9)	3037	3306	
H-H Stretching (ν_3)	2813 (24.8)	2936 (15.9)	2795	2789	

Relative intensities are in parentheses. [a]Reference 10. [b]Reference 11. [d]This work on $CH_5^+(H_2)$

FIGURE CAPTIONS

Fig.1 Mass spectrum showing the carbonium ion CH_5^+ and the solvated carbonium ions $CH_5^+(H_2)_n$(n = 1,2), and other solvated carbonium ions. The mixing ratio CH_4 : H_2 was 1:2000, and the source pressure, the source temperature and the discharge current were 150 torr, -40°C and 20 μA, respectively.

Fig.2 IR spectrum of the CH_5^+ moiety of $CH_5^+(H_2)$ in the 2700 cm^{-1} - 3300 cm^{-1} region, showing a very broad and asymmetric band feature. The bar spectrum at the bottom shows an ab initio prediction spectrum(from ref.10 and ref.11).

Fig.3 IR spectrum of the H_2 moiety of $CH_5^+(H_2)$ in the 4050 cm^{-1} - 4120 cm^{-1} region, showing very clear P, Q, R branches. Two peaks marked with asterisks are attributed to the hot bands. The band origin was determined to be 4077.4 cm^{-1}.

Fig.4 Structure of the $CH_5^+(H_2)$ modelled in this work, shown with the ab initio structure of ^+H which was used for comparison in this work.

Fig.5 (a) Observed IR spectrum of the H-H stretching mode. The rotational lines are assigned with the corresponding rotational J quantum numbers. (b) Simulated spectrum obtained as the best fit to the observed spectrum assuming a prolate top. Rotational constants used in this simulation are as follows: A = 4.2 cm^{-1}, B = C = 0.74 cm^{-1} for the ground vibrational state and A′ = 4.2 cm^{-1}, B′ = C′ = 0.746 cm^{-1} for the excited vibrational state,

and T = 60°K, $\Delta\nu$(FWHM) = 0.4 cm^{-1}.

Fig.6 Expanded spectrum of near Q-branch region of the H-H stretching band, showing significant splitting taking place in each rotational line.

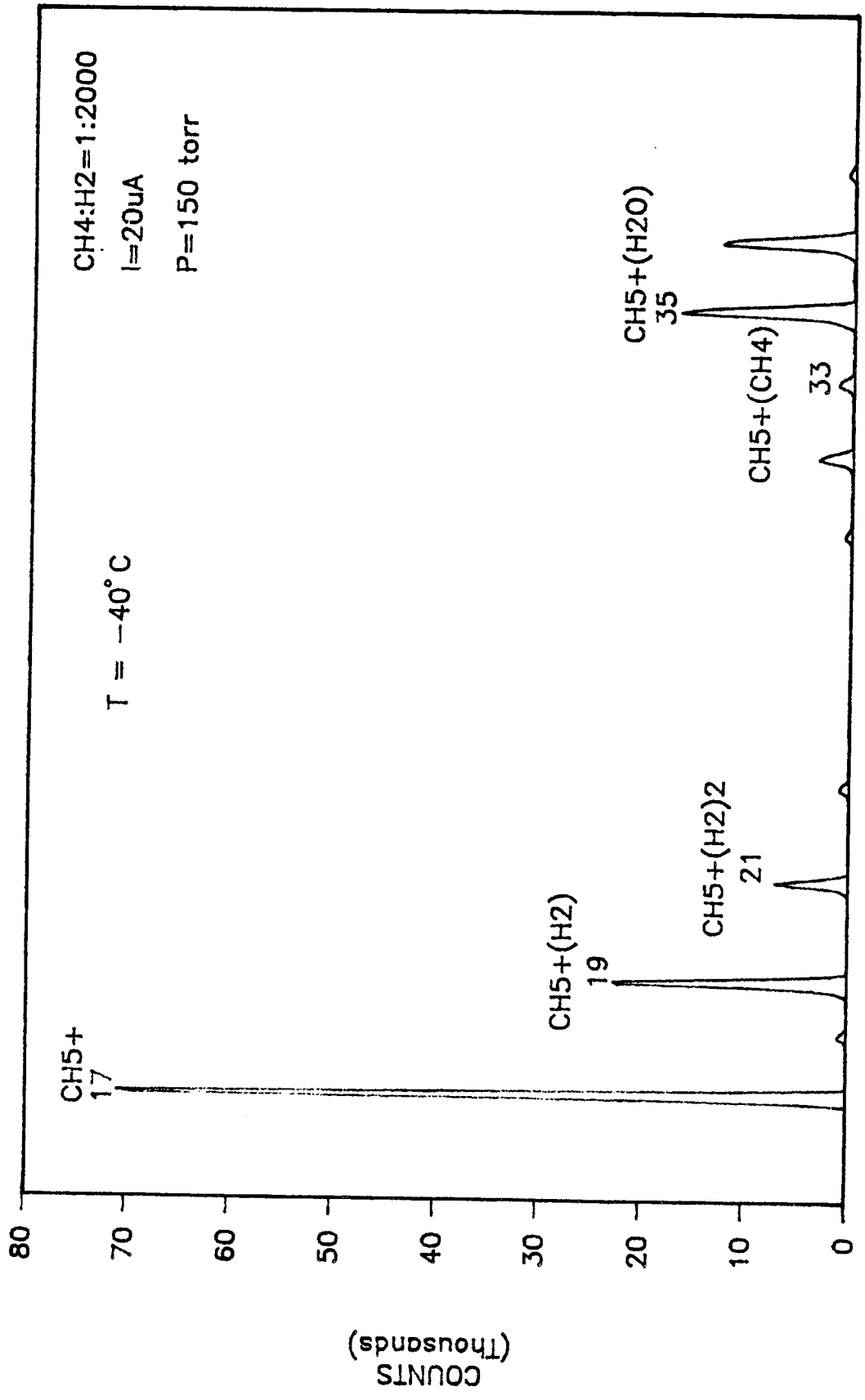

MASS SPECTRUM
CH4:H2=1:2000
I=20uA
P=150 torr
T = −40°C
CH5+
17
CH5+(H2)
19
CH5+(H2)2
21
CH5+(CH4)
33
CH5+(H2O)
35
COUNTS
(Thousands)
80
70
60
50
40
30
20
10
0
MASS

Fig. 1

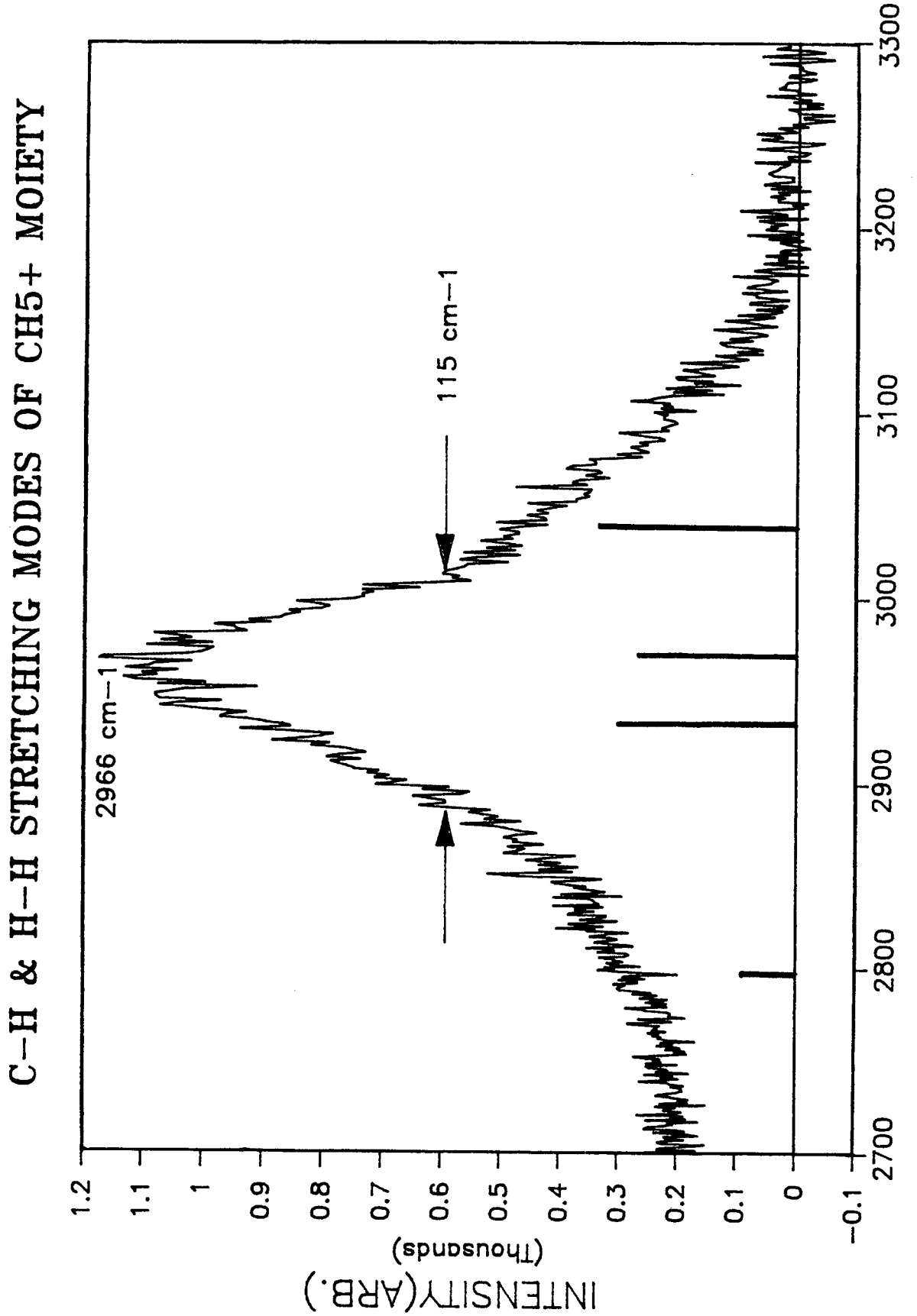

C–H & H–H STRETCHING MODES OF CH5+ MOIETY
2966 cm–1
115 cm–1
INTENSITY(ARB.)
(Thousands)
FREQUENCY, cm–1
1.2
1.1
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
–0.1
2700
2800
2900
3000
3100
3200
3300

Fig. 2

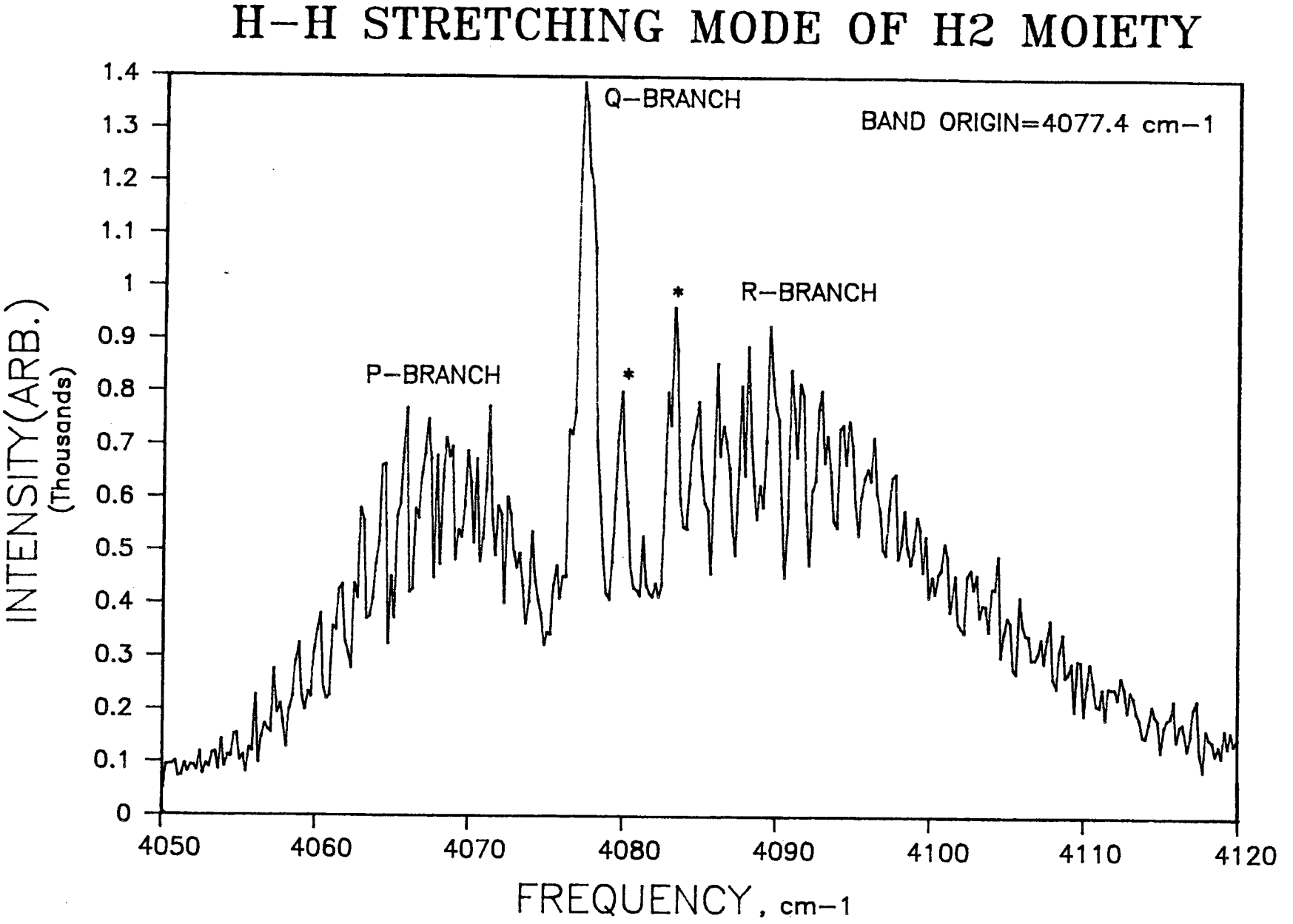
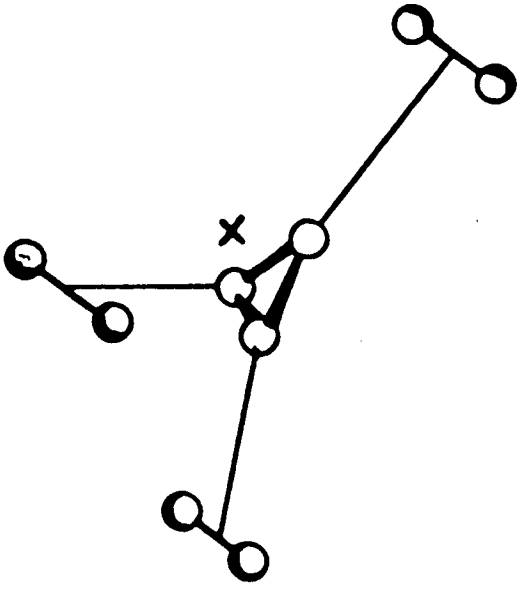

H–H STRETCHING MODE OF H2 MOIETY
Q–BRANCH
BAND ORIGIN=4077.4 cm–1
R–BRANCH
P–BRANCH
*
*
INTENSITY(ARB.)
(Thousands)
1.4
1.3
1.2
1.1
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
4050
4060
4070
4080
4090
4100
4110
4120
FREQUENCY, cm–1

Fig. 3

MODELLING OF $CH_5^+(H_2)$ STRUCTURE

H_9^+



$CH_5^+(H_2)$

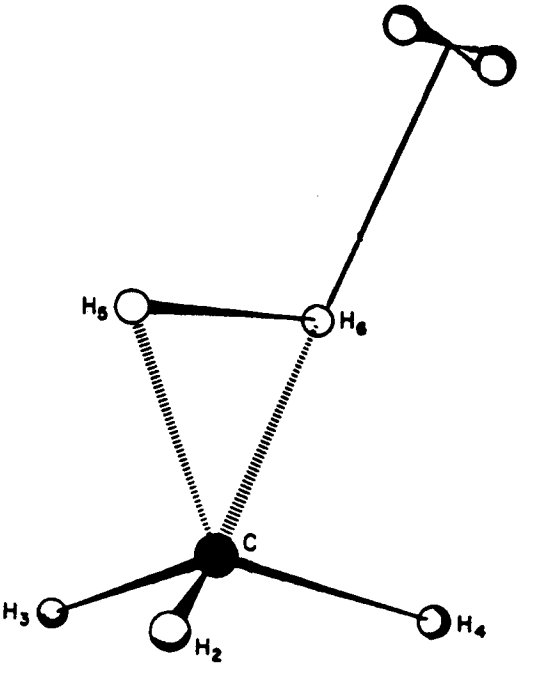


Fig. 4

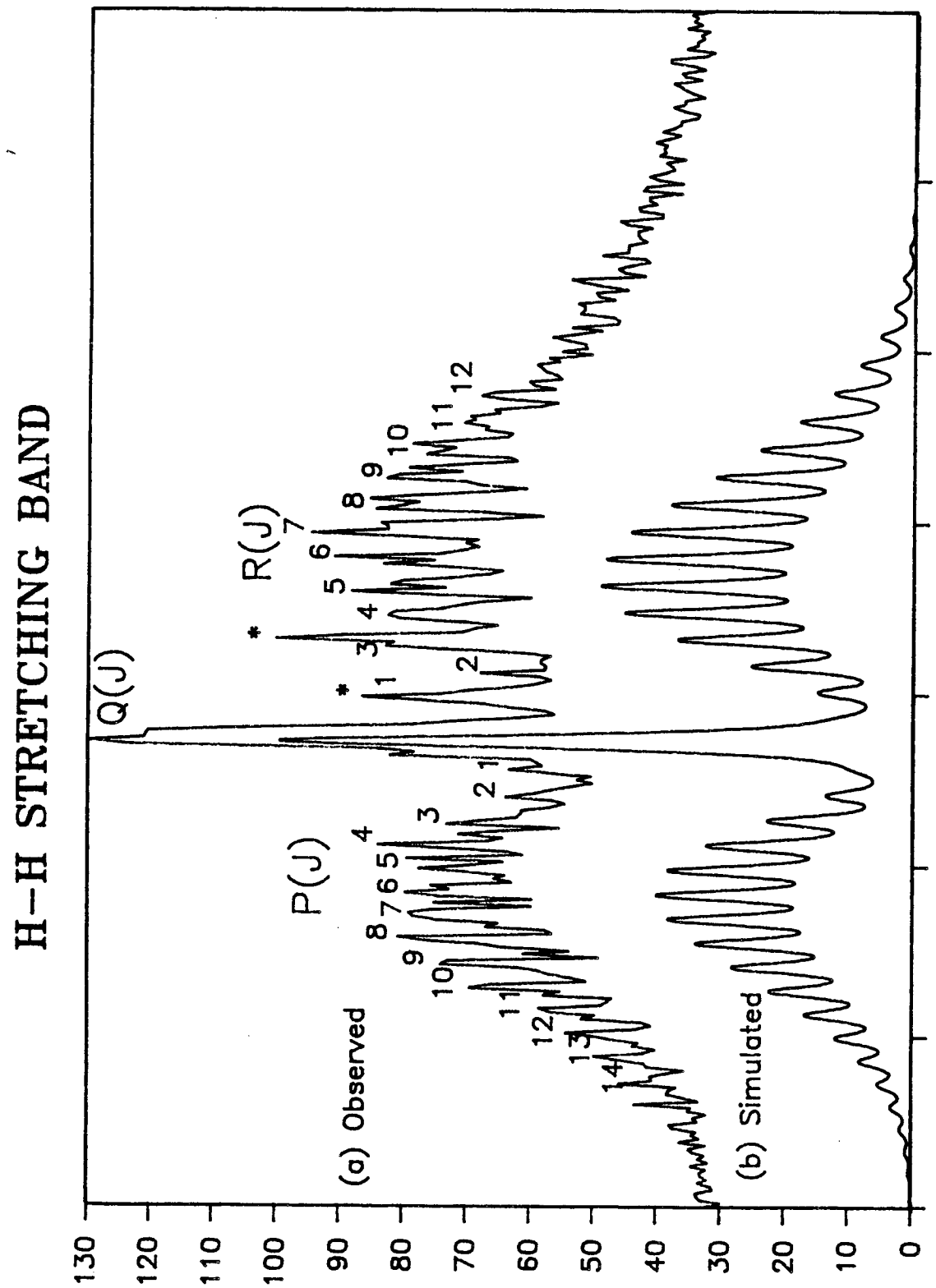

H-H STRETCHING BAND
INTENSITY(ARB.)
FREQUENCY, cm-1
Q(J)
P(J)
R(J)
(a) Observed
(b) Simulated
4050
4059.9
4069.9
4079.9
4089.9
4099.9
4110
0
10
20
30
40
50
60
70
80
90
100
110
120
130

Fig. 5

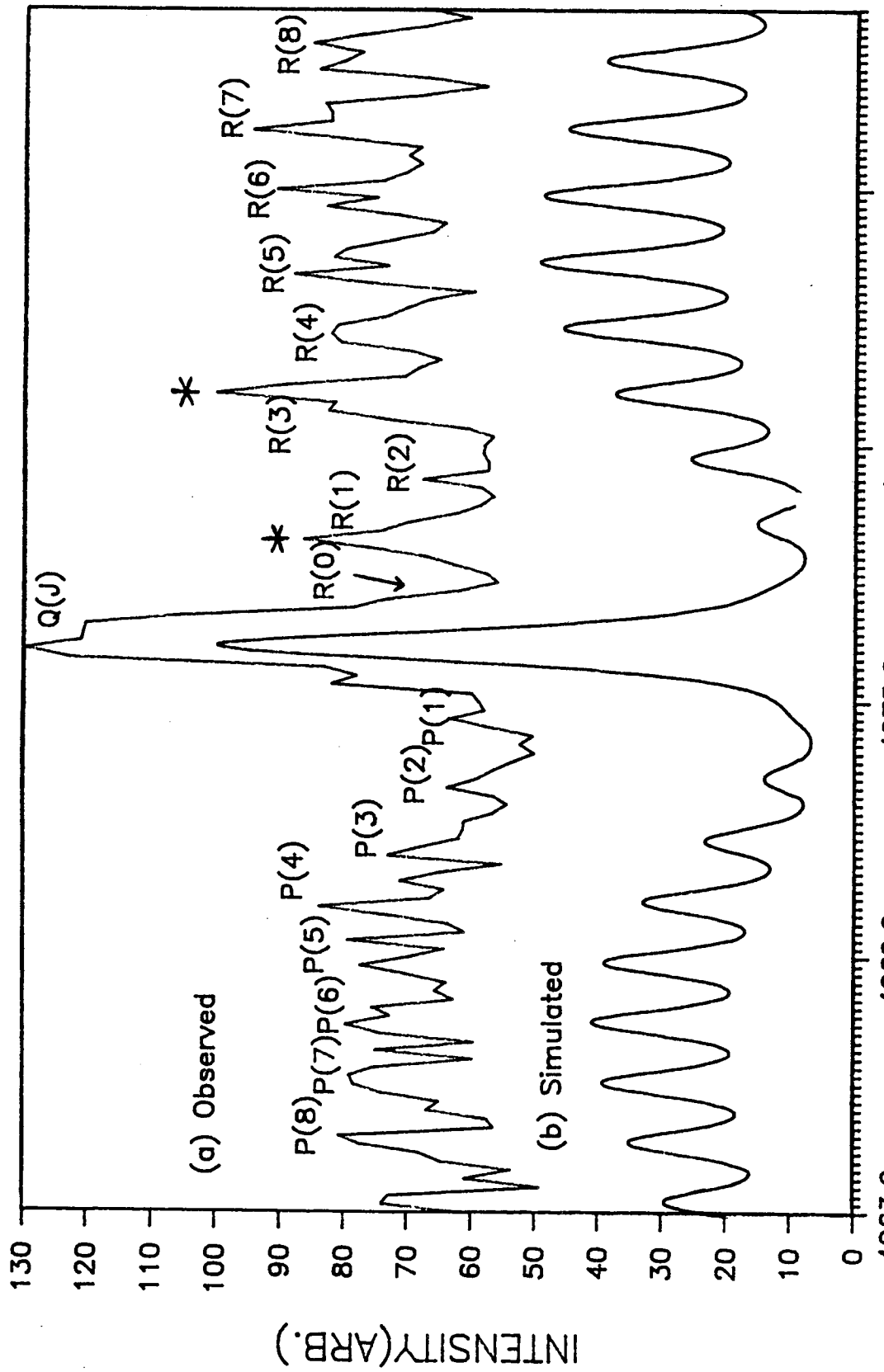

H-H STRETCHING BAND
INTENSITY(ARB.)
FREQUENCY, cm-1
4063.9
4069.9
4075.9
4081.9
4087.9
0
10
20
30
40
50
60
70
80
90
100
110
120
130
(a) Observed
(b) Simulated
Q(J)
R(0)
R(1)
R(2)
R(3)
R(4)
R(5)
R(6)
R(7)
R(8)
P(1)
P(2)
P(3)
P(4)
P(5)
P(6)
P(7)
P(8)

Fig. 6

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